Optimizing Microchannel Reactors by Trading-Off Equilibrium and Reaction Kinetics through Temperature Management

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Abstract

Reversible exothermic chemical reactions exhibit improved reaction kinetics but lower equilibrium conversion with increasing temperature. Consequently, lowering the reaction temperature favors higher conversion but requires more catalyst and results in a larger reactor. Highly effective heat exchange in microchannel reactors makes it possible to not only remove heat of reaction but also reduce the reaction temperature. Therefore, by managing the temperature profile of the reactor, the reactants can be fed at a high temperature where rapid kinetics promotes an initial rapid approach to equilibrium. As the reaction mixture is cooled as it proceeds down the reactor, conversion is increased.

This approach is demonstrated for the Sabatier and Water Gas Shift reactions, illustrating improved conversion and throughput when a temperature profile is maintained in a microchannel reactor. In addition, FEMLAB, a commercial computational fluid dynamics software package, is used with a derived kinetic model for a water-gas-shift catalyst to design a gradient temperature microchannel reactor.

Introduction

Maximizing the reaction temperature is desired for single reactions that are irreversible or endothermic because both kinetics and conversion increase with increasing temperature. However, when dealing with competing reactions or reversible exothermic reactions, a trade-off between kinetics, equilibrium, and selectivities will likely require an optimal temperature trajectory to minimize reactor size and maximize yield for a given conversion. For example, for a single reversible exothermic reaction, such as water-gas-shift, the temperature trajectory would start at a high temperature to take advantage of fast kinetics and proceed to lower temperatures to improve conversion. More complex optimal temperature trajectories are possible with reaction sequences or competing reactions. The work here is focused on single reactions where the optimal trajectory is monotonically decreasing.

One conventional method for improving the temperature trajectory is to employ a sequence of alternating adiabatic reactors and heat exchangers [1]. The inlet temperature of each successive reactor is progressively colder, but the temperature increases down the length of each reactor due to the heat of reaction. Consequently, a plot of the temperature through the sequence is saw-toothed rather than monotonically decreasing. A sequence of two water-gas-shift reactors is the typical approach for fuel processors being developed to produce H_2 from liquid fuels for fuel cell power applications [2]. The reformate is first reacted at about 400°C in the high temperature shift (HTS) followed by a second reactor having an inlet temperature of around 250°C to achieve 90% conversion of the CO to CO_2.

Alternatively, packed-bed reactors with tubular heat exchange have been employed to improve the temperature trajectory for reversible exothermic reactions. The reaction mixture is actively cooled by heat exchange to a fluid flowing on the shell side of the tube bundle. The objective is to achieve the optimal temperature profile in the direction of flow while minimizing temperature gradients in the transverse directions. One example of a tubular heat exchange reactor is the Tennessee Valley Authority ammonia synthesis reactor, which was simulated by Baddour et al. [3]. The reactor consists of an array

of 5 cm OD tubes penetrating through a packed catalyst bed. In this reactor, temperature differences between the hot and cold streams at a given cross-section are on the order of 200°C [3], implying large thermal gradients across the bed.

The superior heat transfer achievable in microchannel reactors is used to advance the ability to optimize temperature profiles of reversible exothermic reactors. By maintaining heat transfer length scales on the order of 100 microns, minimal temperature gradients across the catalyst are maintained while achieving precise control of the temperature profile down the length of the reactor. In addition, the high heat fluxes realized in microchannel heat exchangers facilitate the use of higher activity catalysts. Finally, the lower temperature driving forces that are utilized result in recovery of the heat of reaction at a higher temperature opening up the possibility for increased energy efficiency.

Optimum Temperature Trajectories

The reaction rate for a single reaction with a given catalyst is a function of the feed composition and temperature. The temperature corresponding to the maximum reaction rate, T_{max}, is determined from the partial derivative of the reaction rate with respect to temperature. When expressed in terms of conversion of reactant A, T_{max}, is defined by

$$\frac{\partial r_A\left(x_A, T_{\max}(x_A); C_{i0}\right)}{\partial T} = 0 \tag{1}$$

at a given conversion, x_A, starting from an initial composition, C_{i0}.

The optimum temperature trajectory for the case of an ideal plug flow reactor is determined from the mass balance equation,

$$C_{A0}\, u_s\, \frac{dx_A}{dz} = r_A\left(x_A, T_{\max}(x_A)\right) \tag{2},$$

where C_{A0} is the initial concentration of A and u_s is the flow velocity. Integrating this equation gives the minimum reactor length required to achieve a given level of conversion. Furthermore, the minimum amount of catalyst is calculated from the reaction rate equation.

Water-Gas Shift Reaction

The water-gas-shift reaction is employed in fuel processors that reform liquid fuels to produce hydrogen for fuel cells. The shift reaction increases hydrogen yield while reducing CO, which is a poison for the proton-exchange membrane (PEM) fuel cell anode [4]. The WGS reaction,

$$CO \;+\; H_2O \;\leftrightarrow\; H_2 \;+\; CO_2 \tag{3},$$

is exothermic and reversible. Conventional copper-zinc catalysts have yielded rate equations that are first order in CO and H_2O [5]. We have established that the newer precious metal catalysts are first

order in H_2O only [6]. Simplifying the rate expression by neglecting Langmuir adsorption terms, the rate equation for the precious metal catalyst becomes

$$r_{CO} = \rho_B\, k_{CO}(T)\left(p_{H_2O} - \frac{p_{H_2}\, p_{CO_2}}{K_{eq}(T)\, p_{CO}} \right) \tag{4.}$$

 Where ρ_B is the catalyst loading in g-cat/cm^3, k_{CO} is the reaction rate coefficient in mol CO/s.g-cat.atm, and p_i is the partial pressure of component i. The equilibrium constant dependence on temperature is [7]

$$K_{eq}(T) = \frac{p_{H_2O}\, p_{CO}}{p_{H_2}\, p_{CO_2}} = \exp\left(-4.354 + 4594/T[K]\right) \tag{5.}$$

The kinetic coefficient, k_{CO}, is also expressed as an Arrhenius relationship.

Figure 1 illustrates the dependence of reaction rate on temperature, based on a kinetic model derived from experimental data taken between 225°C and 400°C. The initial composition is representative of a reformate stream generated from steam reforming of isooctane at a 3:1 steam to carbon ratio. The initial maximum reaction rate occurs at 665°C, which is only 70°C colder than the equilibrium temperature. As the reaction proceeds, the peak rate rapidly drops along with the temperature at which the peak rate occurs. The peak rate drops by half after 10% conversion, by almost a factor of 30 at 50% conversion, and by over three orders of magnitude by the time 90% conversion is reached. The reaction rate curves indicate that the size of a reactor to accomplish high conversion and the amount of catalyst required is strongly dependent on the temperature trajectory through the reactor.

Figure 2 illustrates an optimal temperature profile based on the same kinetic relationship and initial composition as used in Figure 1.   As expected, most of the conversion, 82%, occurs in the first third of the reactor, and the remaining two-thirds of the reactor is required for the remaining 8% of conversion, a direct result of much lower activity as the temperature decreases. Furthermore, the optimal temperature profile calls for a rapid decrease in temperature—from 665°C at the inlet to 400°C at eight percent along the axial length of the reactor. This is also where two-thirds of the heat of reaction is being generated adding to the unbalanced heat load at the inlet end of the reactor.
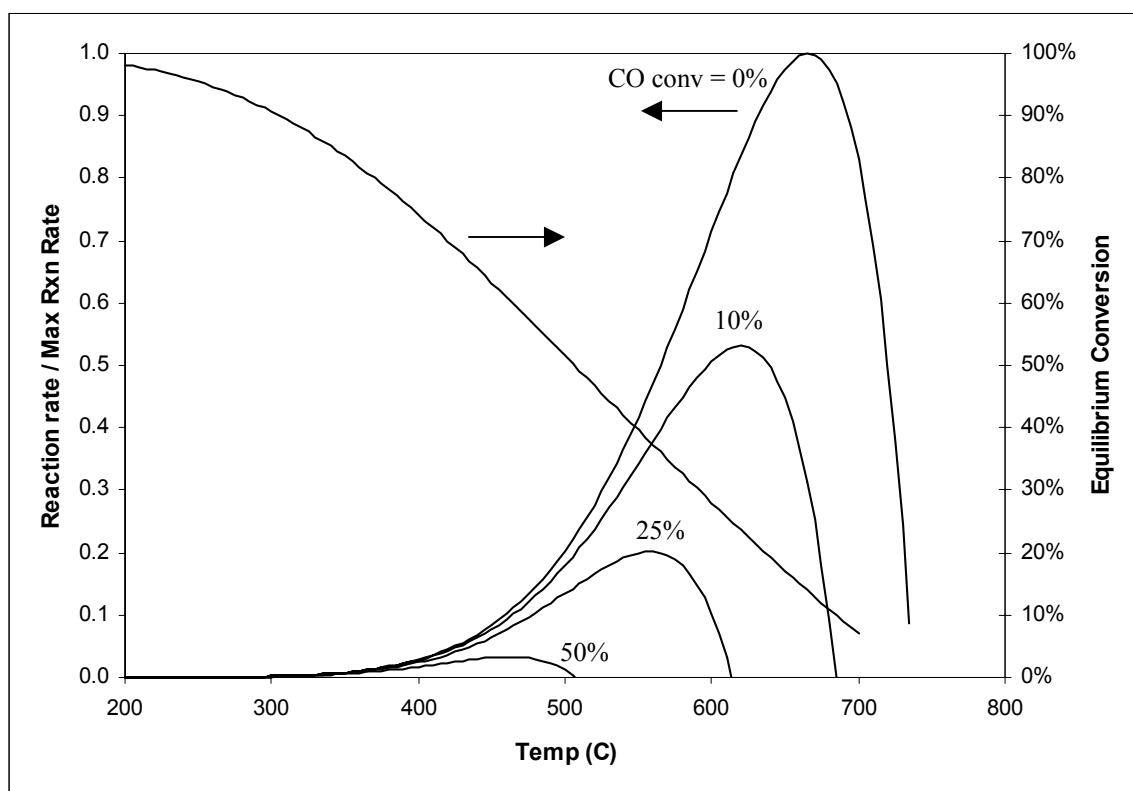
Figure 1. Representative reaction rate curves at various CO conversions starting from a steam reformate feed at an initial composition of 9% CO, 9% CO_2, 36% H_2O, and 45% H_2, along with the equilibrium curve for this starting composition.

Other considerations may impose an upper temperature limit on the inlet. For the water-gas-shift reaction, methane formation, coking, or catalyst sintering may prohibit inlet temperatures as high as 600°C. Conventionally, adiabatic high temperature shift reactors are operated in the 350-450°C range in fuel reformers [2]. When upper limit temperature constraints are imposed, an alternative temperature trajectory is to enter the reactor at the upper limit temperature and operate isothermally through the initial stage of the reactor. Once the optimum temperature drops below the upper limit, then the optimal temperature profile shown in Figure 2 is followed. Integrating Equation 3 for this alternate temperature trajectory gives an increase in reactor size of only 12% for a 90% conversion reactor when starting with the example steam reformate stream. This illustrates that following the optimal temperature profile is more crucial at the cold end of the reactor where the reaction rates are lower.

An alternative configuration for water gas shift of a reformate stream is a sequence of two adiabatic reactors with intercooling, which is a typical approach used in fuel reforming. In this case, reactor productivity is maximized for a given total conversion by optimizing the two inlet temperatures and the amount of conversion in the first reactor. When comparing this configuration to the optimal temperature trajectory for the steam reformate stream and using the same kinetic rate expression, approximately 2.3 times more catalyst is required for 90% conversion in the optimized two-stage adiabatic reactor system than is required if the optimized temperature trajectory is achieved. When the conversion is increased to

93%, the factor increases to 2.5 times more catalyst. Of course, the actual size of the reactor(s) may not be smaller because of the addition of active heat exchange to remove the heat of reaction and cool the reacting gas mixture. However, if the entire system of two reactors plus the intervening heat exchanger is considered, the over all size and mass will be smaller with the optimal temperature profile. The system is also simplified by combining three components into one. In addition, the catalyst may be an important cost element, so improving catalyst productivity may be sufficient alone for pursuing an optimized profile.
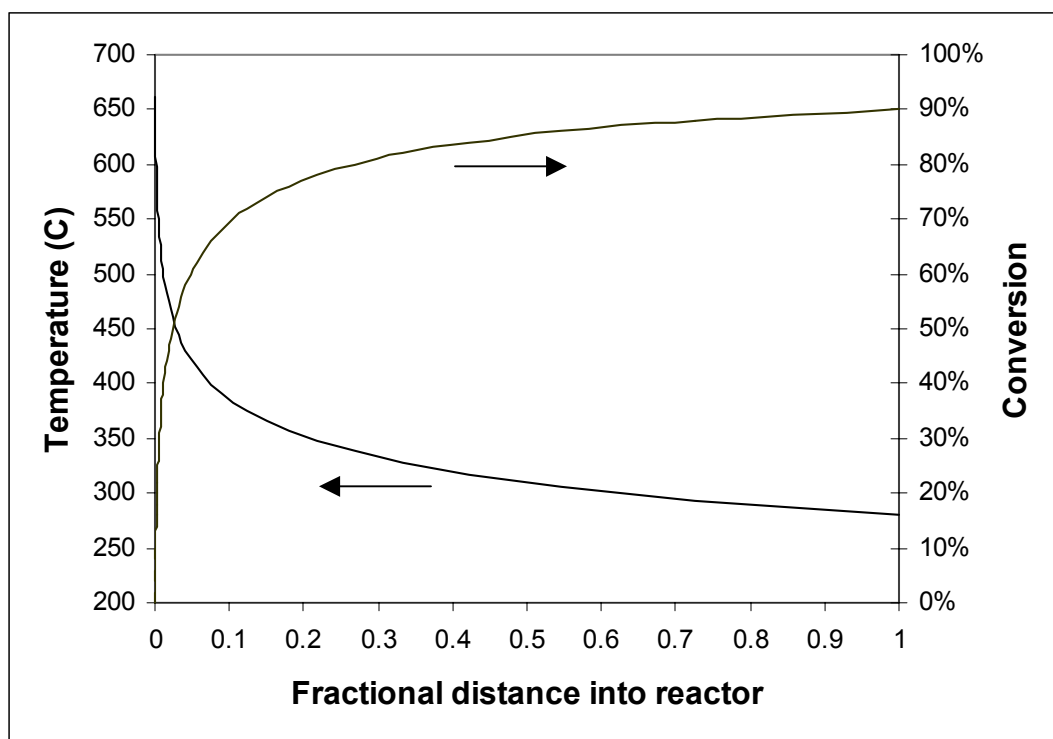

Figure 2. Representative optimum temperature profile and corresponding conversion profile for a water-gas-shift reactor with a steam reformate feed at an initial composition of 9% CO, 9% CO_2, 36% H_2O, and 45% H_2.

Temperature Trajectories in a WGS Microreactor

Microreactors offer the unique advantage of exceptional heat exchange integration within catalytic reactors, particularly with highly exothermic or endothermic reactions [8]. This same advantage can be utilized for approaching optimal temperature trajectories for exothermic, reversible reactions. A schematic for one possible microchannel configuration is shown in Figure 3. Catalytic monoliths are located at the center of an array of reaction flow channels, which are interleaved with heat exchange channels. A heat exchange fluid flowing co-current or counter-current (as shown in Figure 3) to the reaction flow removes the heat of reaction and cools the gas, thereby establishing a temperature trajectory for the reaction. The choice of coolant, the temperature and flow of the coolant, and the geometry are all design variables for achieving an optimal temperature profile to maximize the productivity of the catalyst.
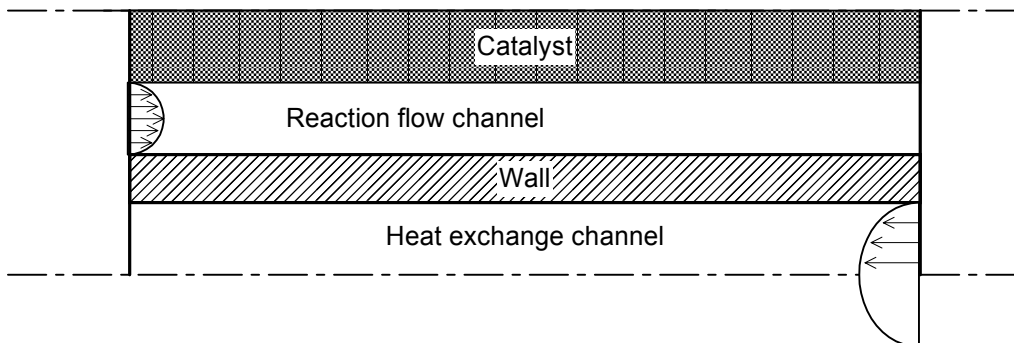
Figure 3. Two-dimensional schematic of a repeat unit for a microchannel reactor with counter-current heat exchange; dashed lines indicate symmetry planes.
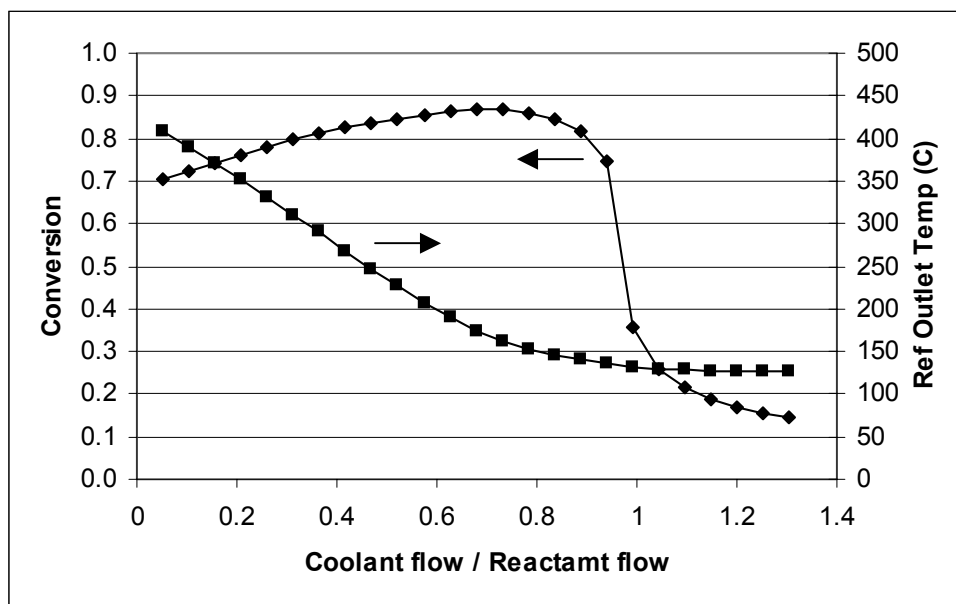

Figure 4. Representative effect of coolant flow rate on CO conversion and reformate outlet temperature for a water-gas-shift microchannel reactor having a constant steam reformate feed at 350°C and an initial composition of 9% CO, 9% CO_2, 36% H_2O, and 45% H_2 and being cooled with 125°C air.

A water-gas-shift reactor having the geometry depicted in Figure 3 was modeled using the Femlab[®] software package, a PDE-based multiphysics modeling tool. Using a two-dimensional model, the convective, diffusion differential equations were solved in the catalyst and reaction flow domains, while the convective, conduction equation were solved in all four domains. The flow fields in the reaction flow channel and the heat exchange channel were specified as parabolic with specified inlet temperatures. The convective, diffusion equation was solved in terms of conversion, with zero conversion specified as a boundary on the inlet of the reactant flow channel. The two symmetry planes and all other external boundaries were specified with no flux conditions for both heat and mass transfer.

Figure 4 provides an example of the potential for increasing conversion of a reversible, exothermic reaction with active cooling in microchannels. In this example, the steam reformate feed to a microchannel WGS reactor is kept at constant flow rate and inlet temperature of 350°C, while increasing the flow of 125°C air as coolant. At very low coolant flow, the reactor is essentially adiabatic, and the reaction mixture increases to over 400°C, where the conversion is limited to 70%. However, as the coolant flow is increased, the reformate outlet temperature decreases allowing the CO conversion to increase to maximum of 87%. However, if the coolant flow is increased further, the reaction mixture is cooled too quickly before substantial conversion can occur, effectively quenching the reaction. The high effectiveness of heat exchange possible in microchannel reactors allows for relatively small approach temperatures. At the maximum conversion, the reformate exits at 174°C, a 49°C approach temperature at the cold end, and the coolant exits at 398°C, hotter than the incoming reformate stream. The abiility to capture the heat of reaction at a higher temperature also creates the potential to improve overall system efficiency when thermally integrated.

In fact, the heat exchange in the example shown in Figure 4 is too effective as indicated by an outlet reformate temperature of 174°C, which is well below the optimum reaction rate temperature. Consequently, CO conversion would benefit by reducing the heat transfer coefficient or by increasing the temperature of the coolant. The latter effect is demonstrated in Figure 5. Again the reformate flow rate and inlet temperature are constant and the amount of coolant flow rate is increased for three different coolant temperatures. In this case, the maximum conversion increases by 2.7% when the heat exchange fluid temperature is increased from 125°C to 225°C.

Obviously, lowering the reactant flow rate will increase CO conversion but decrease reactor productivity. The other variable to consider is the inlet temperature of the reactant flow. Increasing the starting temperature will increase initial reactivity but also increase the heat exchange duty. Figure 6 illustrates the effect of reactant feed temperature at a constant reactant feed flow rate and a coolant temperature of 225°C. There is a negligible effect on the maximum conversion that can be achieved, but the potential for quenching the reaction is much stronger at the lower feed temperature.

Several operating parameters have been explored for a specific reversible exothermic reaction, kinetic rate expression, and geometry. Ultimately, a microchannel reactor design to achieve an optimal reaction temperature trajectory would depend not only on the specific reaction and catalysis, but also on system considerations, such as thermal integration, start-up, turn-down, and dynamic response.
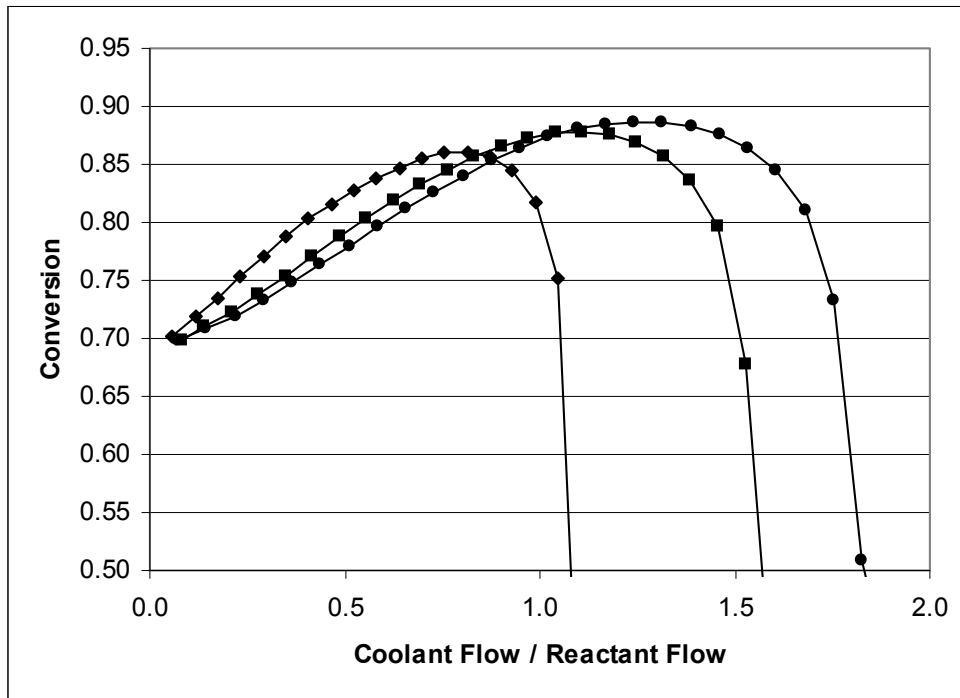
Figure 5. Representative effect of coolant temperature on CO conversion for a water-gas-shift microchannel reactor having a constant steam reformate feed at 350°C and an initial composition of 9% CO, 9% CO_2, 36% H_2O, and 45% H_2; results shown for 125°C coolant (◆), 200°C (■), and 225°C (●).
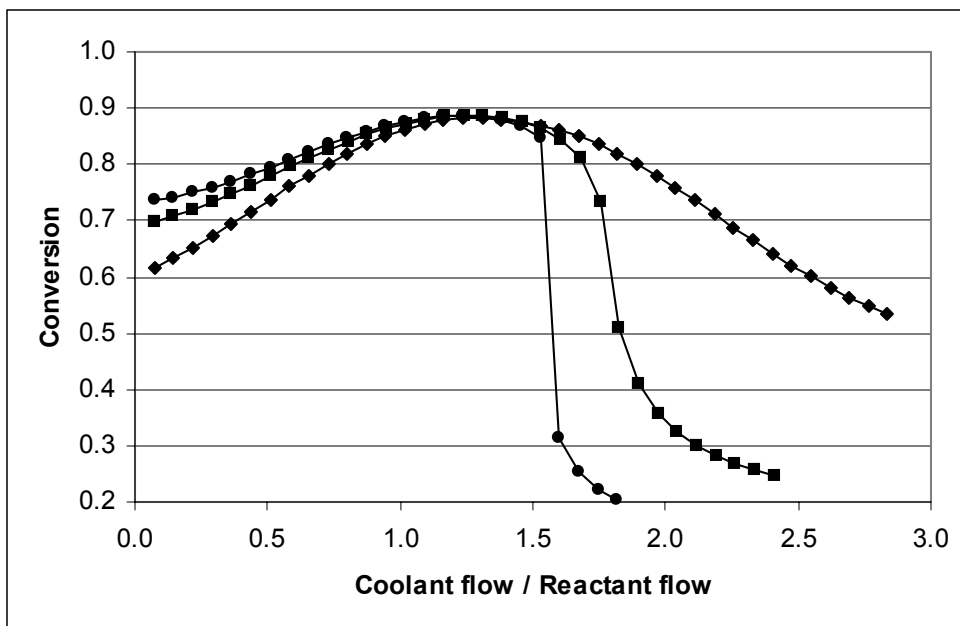

Figure 6. Representative effect of reactant inlet temperature on CO conversion for a water-gas-shift microchannel reactor having a constant steam reformate feed flow and an initial composition of 9% CO, 9% CO_2, 36% H_2O, and 45% H_2 and being cooled with 225°C air; results shown for 400°C coolant (◆), 350°C (■), and 325°C (●).

9

Sabatier Reaction

Another reversible, exothermic reaction is the Sabatier reaction of hydrogen and carbon dioxide. This reaction is of interest for producing propellant on the surface of Mars from the atmospheric carbon dioxide [9] Having to transport only hydrogen or water from earth instead of all the propellant for the return trip has the potential for substantial savings in launch mass for both sample return and manned missions to Mars [10]

The Sabatier reaction,

$$CO_2 \; + \; 4H_2 \; \leftrightarrow \; 2H_2O \; + \; CH_4 \tag{6},$$

is an exothermic reaction with a 165 kJ/mol CO_2 heat of reaction at 25°C. Carbon monoxide is a byproduct formed by the reverse-water-gas shift reaction. Both the conversion and possibly selectivity can be enhanced by operating a microreactor with an optimal temperature trajectory.

The principle is illustrated with data from a N_2-cooled, counter-current microchannel reactor. A mixture of 20% CO_2 and 80% H_2 is fed to a microreactor at 400°C. If allowed to proceed adiabatically to equilibrium the temperature would rise to 625°C, limiting the conversion to 66% of CO_2 and selectivity for methane over carbon monoxide would drop to 41.6%. Alternatively, isothermal operation would allow the conversion to increase to as high as 85% with methane selectivity 99.4%. Data shown in Figure 7 illustrate how adiabatic conversion is exceeded with active cooling in a microreactor. At the highest contact time, calculated as the reactor volume divided by the standard state feed flow rate, the isothermal conversion is exceeded slightly. Proceeding to longer contact times with additional cooling would generate a temperature profile giving even higher conversions.

Conclusions

In the past, microchannel architectures have made it possible to very effectively supply heat to highly endothermic reactions and to control temperature for highly exothermic reactions. Here, the capability to control temperature is taken a step further by describing how precise management of the temperature profile with microchannel heating and cooling can greatly enhance the conversion and productivity of catalysts and reactors. The consequence is increased process intensification and more compact hardware. This is most obviously beneficial for reversible, exothermic reactions but is also applicable with more complex reaction schemes, such as reaction sequences and with competing reactions. The full potential for an optimal temperature profile is realized by the extremely short distances for heat and mass transfer. Furthermore, high thermal effectiveness that is possible with microchannels allows superior heat recovery to higher temperatures, thereby opening up opportunities for better thermal integration and higher overall energy efficiency.
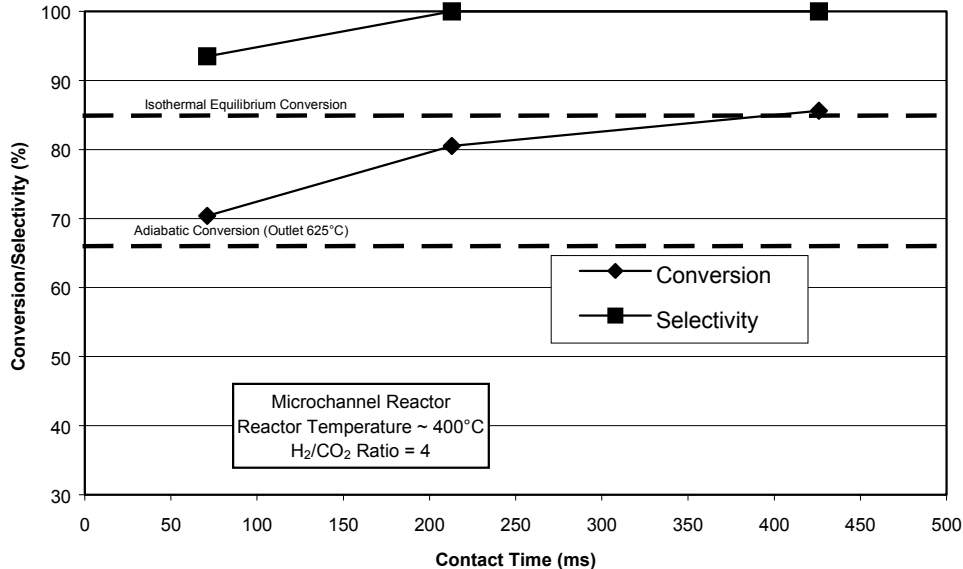
Figure 7. Conversion and selectivity results from the Sabatier reaction with a N_2-cooled, counter-current microreactor compared to equilibrium results at isothermal and adiabatic conditions.

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